

Thermochemistry of solutions of biochemical model compounds.

7. Aqueous solutions of some amides, t-butanol and pentanol ^a

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^a Part 6, see reference 1.

Abstract

Enthalpies of solution in water at infinite dilution have been determined at 298.15 K for formamide, N-methylformamide, acetamide and t-butanol. Corresponding partial molar heat capacities were determined for these compounds and for N-methylacetamide, N-butylacetamide, N-methylpentanamide and pentanol using a drop heat capacity calorimeter. Heat capacities for the pure compounds were also determined.

1. Introduction

In the preceding papers of this series thermochemical data have been reported for solutions of several groups of simple organic compounds. The purpose of these studies has been to obtain thermodynamic information, in particular aqueous partial molar heat capacities, which may assist in the understanding of thermochemical results for more complex systems, such as those dealt with in biochemistry.

We report here results from calorimetric measurements on a few amides and on t-butanol and pentanol. Aqueous enthalpies of solution at infinite dilution, $\Delta H_{\text{soln}}^{\infty}$, corresponding partial molar heat capacities, $C_{p,2}^{\infty}$, and the heat capacities for the pure compounds, C_p^* , have been derived at 298.15 K. The choice of the compounds investigated here has mainly been governed by our need for some supplementary data in connection with a discussion⁽²⁾ on additivity relationships for aqueous heat capacities of nonionic compounds.

2. Experimental

MATERIAL

Formamide (Merck analytical grade; 99.5 per cent) was further purified by fractional freezing out three times. The product was dried with 4A molecular sieves and was fractionally distilled under N_2 at reduced pressure. N-methylformamide (EGA-Chemie; 99 per cent) was further purified by drying with molecular sieves and fractional distillation. N-methylacetamide and N-butylacetamide were from reference 3 and N-methylpentanamide was from reference 4. The purities of the amides was tested by g.l.c. (Chromosorb 103; carbowax 400/10 per cent KOH). No traces of

organic impurities were found. The water content was <0.03 mass per cent as determined by g.l.c. Acetamide (EGA-Chemie KG; zone melted, 99.9 per cent) was used as received.

Samples of t-butanol and pentanol were the same as those used in reference 5. Water contents were <0.02 mass per cent.

CALORIMETRY

Enthalpies of solution were determined with a modified LKB Precision Calorimeter. The instrument and working procedure have been described elsewhere.⁽⁶⁾ The reaction vessel was charged with 100 cm^3 of water and the glass ampoules were filled under a dry N_2 atmosphere. Where necessary small corrections were applied to the calorimetric results in order that the ΔH_{soln} values refer to the nominal temperature of 298.15 K. For t-butanol the measurements were performed at 299.15 K in order to keep the compound in the liquid state.

Heat capacity measurements were performed with a double drop heat capacity calorimeter.⁽⁷⁾ About 0.6 cm^3 of the pure compounds or their aqueous solutions were loaded into the stainless steel ampoule. The ampoules were temperature equilibrated at 302.85 K in the 'furnace' before they were transferred to the calorimeter which was kept at 293.40 K. The mean temperature was in all cases $298.15 \pm 0.03\text{ K}$. An empty reference ampoule was simultaneously dropped with the sample ampoule into the calorimeter. Small corrections were applied to the measured heat capacities.⁽⁷⁾

Uncertainties in the values obtained for $\Delta H_{\text{soln}}^\infty$ and C_p^x are expressed as twice the standard deviation of the mean ($\pm 2\text{ sdm}$) except for the small series of enthalpy measurements ($n < 4$) which are estimates. Uncertainties in the partial specific heat capacities for the drop calorimetric measurements were determined by the linear regression method.⁽⁸⁾

3. Results

ENTHALPIES OF SOLUTION

Enthalpies of solution measurements were performed with different quantities of the compounds giving final concentrations of 0.01 - 0.05 mol dm⁻³. For each compound 3-6 determinations were made. For t-butanol (6 experiments) the enthalpy values increased linearly with concentration

($\frac{\partial \Delta H_{\text{soln}}}{\partial c} = (3 \pm 1) \text{ kJ dm}^3 \text{ mol}^{-2}$) and $\Delta H_{\text{soln}}^{\infty}$ (299.15K) was obtained by extrapolation to zero concentration. The $\Delta H_{\text{soln}}^{\infty}$ value was corrected to 298.15 K. For the other compounds no concentration dependency was found and their mean values were taken as $\Delta H_{\text{soln}}^{\infty}$. Values for $\Delta H_{\text{soln}}^{\infty}$ are summarized in table 1 where references are also given to earlier work.

Inspection of table 1 shows that the present $\Delta H_{\text{soln}}^{\infty}$ value for formamide agrees well with the earlier values reported by Stimson and Schrier⁽⁹⁾ and by Arnett and McKelvey,⁽¹⁰⁾ whereas our value for acetamide is significantly higher than those given in references 9 and 10. Stimson and Schrier⁽⁹⁾ have also measured $\Delta H_{\text{soln}}^{\infty}$ for N-methylformamide and found a somewhat higher value than that obtained here. The present $\Delta H_{\text{soln}}^{\infty}$ value for t-butanol is very close to the value reported by Arnett et al.⁽¹¹⁾ and the agreement with the value by Alexander and Hill⁽¹²⁾ is fair.

HEAT CAPACITIES

Five or more heat capacity measurements were made on the aqueous solutions of each compound in the concentration range 0.5 to 2.0 mass per cent. The relationship between the directly measured values for the specific heat capacities and the partial specific heat capacities is given by

$$(1 + W_2) \cdot c_p = c_{p,1} + W_2 \cdot c_{p,2} \quad (1)$$

where W_2 is the weight ratio of solute to solvent, c_p is the measured specific heat capacity, and $c_{p,1}$ and $c_{p,2}$ are the partial specific heat capacities for the solvent and solute, respectively.⁽¹³⁾ Thus, the slope of a plot of $(1 + W_2) c_p$ versus W_2 gives the partial specific heat capacity of the solute and the intercept gives $c_{p,1}$.

In all cases straight lines were obtained which were evaluated by the method of least squares. The intercepts ($W_2 = 0$) were within estimated uncertainty limits equal to the specific heat capacity of water. The values derived for the partial molar heat capacities of the solutes, $C_{p,2}^\infty$, and molar heat capacities for the pure compounds, C_p^* , are summarized in table 1 together with results of previous studies.

For N-methylacetamide, mp ca 304 K, C_p^* is difficult to measure close to the melting point for this very hygroscopic compound. The value was estimated from a comparison with C_p^* values for other liquid compounds of the type $RNHCOR'$, where R,R' are straight chain alkyl groups or hydrogen atoms. These values, which were determined in the present study or previously,⁽⁴⁾ are shown in figure 1 where they are plotted versus the number of alkyl carbon atoms, n. It is seen that a good linear relationship is obtained, the only exception being the value for n=0 (formamide). The equation for the line was derived by the method of least squares

$$C_p^* = A + B \cdot n \quad (2)$$

where n is the number of alkyl carbon atoms. (The value for n=0 was not included in the derivation.)

The value for N-methylacetamide (n=2) was taken to be $C_p^* = 151.4 \text{ J K}^{-1} \text{ mol}^{-1}$. (The statistical uncertainty is $\pm 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$.⁽⁸⁾)

The new C_p^* determination for N-methylpentanamide was initiated because the old value (table 1) deviates considerably from the expected value.

Our C_p^x value for t-butanol (liq) is considerably lower than the value reported by Parks and Anderson⁽¹⁴⁾ (at 300 K), but agrees very well with the value obtained by fitting a least squares second degree polynomial to the data given by Oetting⁽¹⁵⁾ and extrapolating to 298.15 K. The present C_p^x value for n-pentanol is in full agreement with the literature value.⁽¹⁶⁾

The present $C_{p,2}^\infty$ value for N-methylacetamide is significantly higher than the value derived from results of the solution calorimetric measurements by Kreis and Wood.⁽¹⁷⁾ Our $C_{p,2}^\infty$ value for acetamide is in fair agreement with a value reported recently by Kiyohara et al.⁽¹⁸⁾ The earlier $C_{p,2}^\infty$ value reported from this laboratory for N-butylacetamide⁽⁴⁾ is lower than the present value (consideration of additivity rules⁽²⁾ for $C_{p,2}^\infty$ suggested to us that the earlier value was low, which initiated the new determination).

Similarly our empirical additivity rules⁽²⁾ suggested that the literature $C_{p,2}^\infty$ value for pentanol was too high which is verified by the present determination. The present value agrees within uncertainty limits with the very precise value recently determined by Jolicoeur and Lacroix.⁽¹⁹⁾ For t-butanol the present $C_{p,2}^\infty$ value is significantly lower than the earlier values but is in good agreement with the results obtained by Jolicoeur and Lacroix.⁽¹⁹⁾

4. Discussion

HEAT CAPACITIES

Heat capacities for simple organic compounds in aqueous solution are of significant biochemical interest as they are believed to reflect "hydrophobic interactions". In the following paper⁽²⁾ additivity relations for aqueous $C_{p,2}^\infty$ values for several groups of nonionic compounds will be discussed in some detail.

In the first report of this series⁽⁴⁾ it was shown that for the amide and the alcohol series, as well as for amines and carboxylic acids, aqueous $C_{p,2}^{\infty}$ values increased essentially linearly with the number of alkyl carbon groups, n . Branching of the alkyl chain and the nature of the functional group appeared to effect the $C_{p,2}^{\infty}$ values only marginally. In figure 2 the present and earlier⁽⁴⁾ $C_{p,2}^{\infty}$ values for straight chain members of the amide series are plotted versus n . It is seen that an almost straight line is obtained with intercept ($n=0$) $(76.7 \pm 6.5) \text{ J K}^{-1} \text{ mol}^{-1}$ and slope $(88.7 \pm 2.0) \text{ J K}^{-1} \text{ mol}^{-1}$ per alkyl carbon. It was noted earlier⁽²⁰⁾ that for alcohols and carboxylic acids, $C_{p,2}^{\infty}$ values extrapolate to a value at $n=0$ which is rather close to the actual value for water and formic acid, respectively. We find here, figure 2, that for $n=0$ the amide line is very close to the experimental value for formamide.

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TABLE 1. Enthalpies of solution in water at infinite dilution, $\Delta H_{\text{soln}}^{\infty}$, molar heat capacities, C_p^{∞} , and partial molar heat capacities, $C_{p,2}^{\infty}$, for some amides and alcohols at 298.15 K

Compound	$\Delta H_{\text{soln}}^{\infty}/\text{kJ mol}^{-1}$		$C_p^{\infty}/\text{J K}^{-1} \text{ mol}^{-1}$		$C_{p,2}^{\infty}/\text{J K}^{-1} \text{ mol}^{-1}$	
	This work	Earlier work	This work	Earlier work	This work	Earlier work
HCONH ₂ (liq)	2.03 ± 0.01	2.01 ± 0.04 ^a 2.03 ± 0.01 ^b	107.62 ± 0.04	108.1 ± 0.5 ^c	82 ± 1	
HCONHMe(liq)	-7.083 ± 0.005	-7.14 ± 0.02 ^b	123.8 ± 0.2	126.1 ± 0.7 ^c	164 ± 2	
MeCONH ₂ (s)	9.74 ± 0.01	9.54 ± 0.13 ^a 9.644 ± 0.008 ^b	90.3 ± 0.2		160 ± 1	163.8 ± 1 ^d
MeCONHMe(liq)		-13.09 ± 0.02 ^e	151.4 ^f		258 ± 3 ^g	236 ^h
MeCONHBu(liq)		-14.72 ± 0.03 ⁱ		236 ± 1 ⁱ	516 ± 1	506 ± 5 ⁱ
BuCONHMe(liq)		-15.03 ± 0.02 ⁱ	238.4 ± 0.1	229 ± 1 ⁱ	524 ± 4 ^j	515 ± 5 ⁱ
t-BuOH(liq)	-17.44 ± 0.02	-17.46 ± 0.06 ^k -17.31 ± 0.14 ^l	218.6 ± 0.5	225 ^m 219.0 ± 0.1 ⁿ	463 ± 6	484 ± 2 ^l 502 ± 17 ^k 464 ± 0.6 ^o
PeOH(liq)		-7.82 ± 0.05 ^k	208.40 ± 0.08	209 ^p	530 ± 7	559 ± 22 ^k 523.8 ± 0.3 ^o

Notes to table 1

- a) reference 10
- b) reference 9
- c) reference 21
- d) reference 18
- e) from data in reference 17, cf. reference 3
- f) extrapolated value, cf. text
- g) this value was determined by Dr. N. Nichols
- h) calculated from the $\Delta C_{p,\text{soln}}^{\infty}$ value (at 303.71 K) reported in reference 17 and the present $C_p^{\times}$ value
- i) reference 4
- j) calculated from the earlier $\Delta C_{p,\text{soln}}^{\infty}$ value⁽⁴⁾ and the present value for $C_p^{\times}$
- k) reference 11
- l) from data in reference 12. $C_{p,2}^{\infty}$ is derived using our $C_p^{\times}$ value
- m) reference 14, refers to 300 K
- n) reference 15, assigned error in the extrapolated value is estimated, cf. text
- o) reference 19
- p) reference 16, uncertainty ≤ 1 per cent

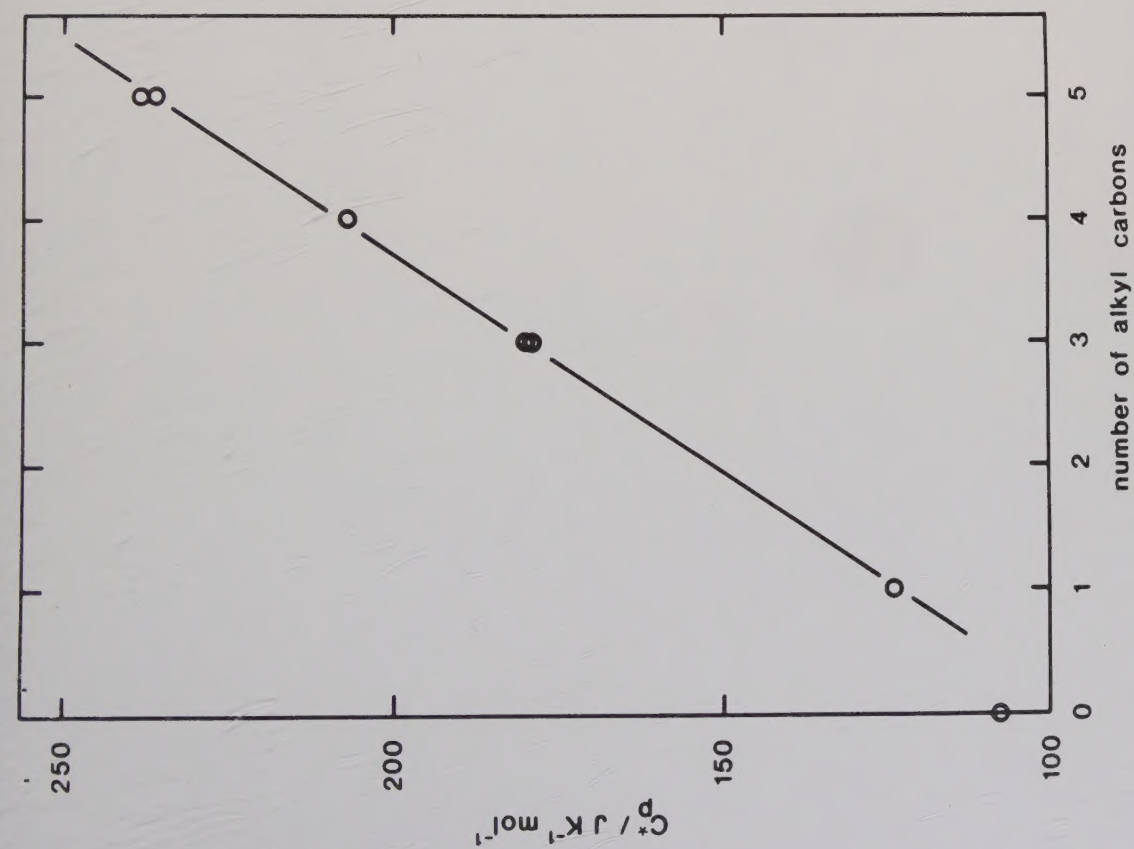


Figure 1

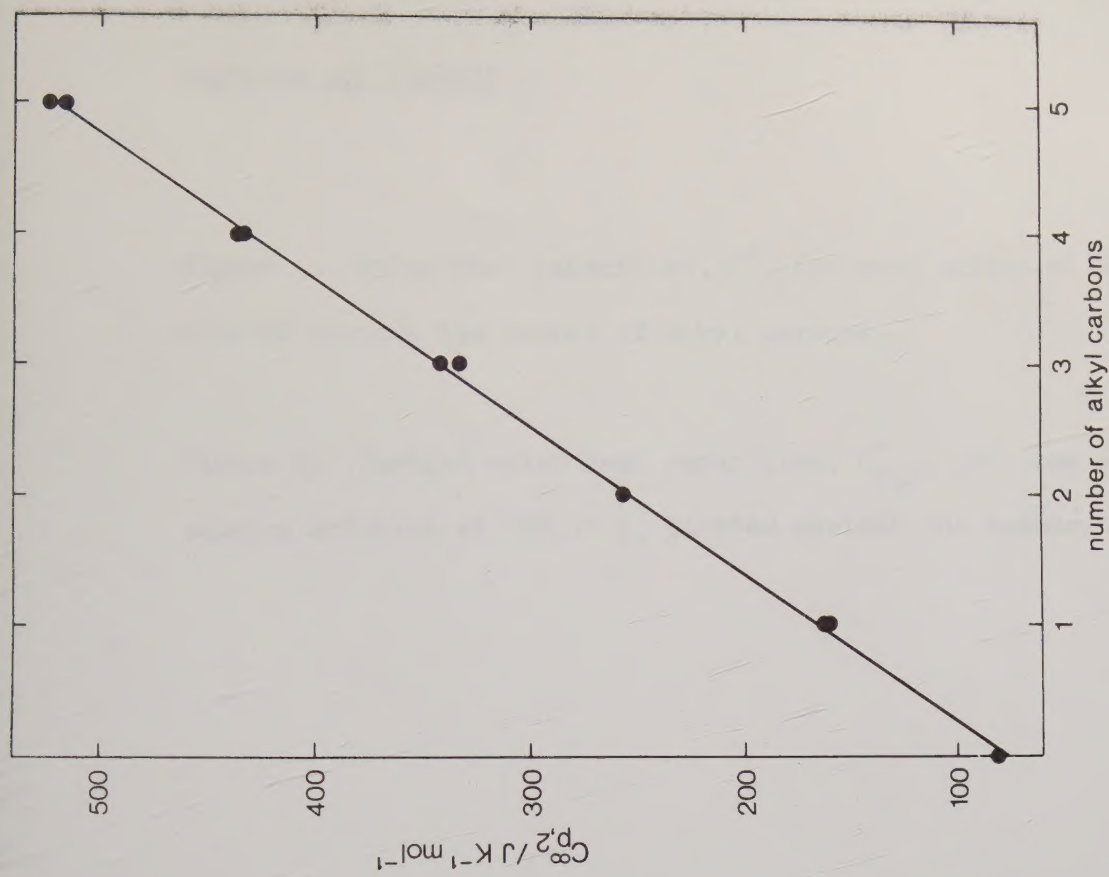


Figure 2

Captions for figures

Figure 1. Molar heat capacities, C_p^x , for some amides at 298.15 K, plotted against the number of alkyl carbons.

Figure 2. Partial molar heat capacities, $C_{p,2}^\infty$, for some amides in aqueous solution at 298.15 K, plotted against the number of alkyl carbons.

